



Effect of benzotriazole derivatives on the corrosion and dezincification of brass in neutral chloride solution

R. RAVICHANDRAN¹, S. NANJUNDAN² and N. RAJENDRAN^{1*}

¹Department of Applied Sciences and Humanities, M.I.T. Campus, Anna University, Chennai 600044, India

²Department of Chemistry, Anna University, Chennai 600025, India

(*author for correspondence, e-mail: nrajendran@annauniv.edu)

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Abstract

The effect of novel corrosion inhibitors, benzotriazole derivatives namely *N,N*-dibenzotriazol-1-ylmethylamine (DBMA), and 2-hydroxy ethyl benzotriazole (HEBTA) on the corrosion and dezincification of a 65/35 brass in 3% NaCl has been investigated by weight-loss, potentiodynamic polarization, electrochemical impedance and solution analysis techniques. Polarization studies clearly indicated that the benzotriazole derivatives behave as anodic inhibitors for brass in chloride solutions. They decrease the anodic reaction rate more strongly than the cathodic reaction rate and render the open circuit potential of brass more positive in NaCl solutions. Solution analysis revealed the decrease in dissolution of both copper and zinc in the presence of these inhibitors.

1. Introduction

Copper alloys represent an important category of non-ferrous alloys, which are widely used as materials in various cooling water systems [1–3]. Brass has been widely used for shipboard condensers, power plant condensers and petrochemical heat exchangers [4–7]. Dezincification of brass is one of the well-known and common processes by means of which brass loses its valuable physical and mechanical properties leading to structural failure. Organic compounds containing an azole nucleus have been found effective inhibitors for copper alloys in a variety of aggressive environments [8, 9].

The action of benzotriazole (BTA) as a corrosion inhibitor for copper and its alloys in aqueous chloride media has long been of great interest to corrosion scientists and numerous studies have been performed [10–14]. The effectiveness of BTA has been related to the formation of a $[\text{Cu}^+\text{BTA}^-]_n$ film at low pH and positive electrode potential, the film is considered as being insoluble and polymeric [15, 16]. Schweinsberg et al. [17, 18] had done an extensive research on the action of benzotriazole and its derivatives for copper corrosion in acidic solution. Bag et al. [19] investigated the protective action of azole derivatives on the corrosion and dezincification of 70/30 brass in ammonia solution and concluded that the inhibitors effectively control corrosion. Walker [20] has shown that the addition of small amounts of 1,2,3-benzotriazole and 1,2,4-triazole inhibit the corrosion of brass in various acidic, neutral and

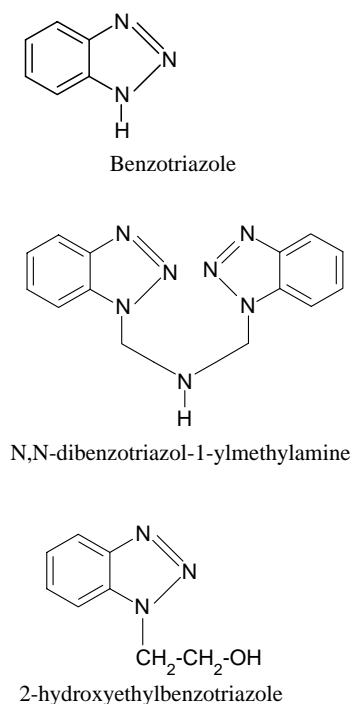
alkali solutions at ambient temperature. Mansfeld et al. [21] also reported that corrosion of copper in sodium chloride solution could be halted by the presence of BTA.

The aim of the present investigation was to study the inhibition efficiencies of benzotriazole, *N,N*-dibenzotriazol-1-ylmethylamine and 2-hydroxy ethyl benzotriazole on the corrosion and dezincification of 65/35 brass in 3% NaCl media. Interest in chloride media relates to the applicability of brass as the tubing material for condensers and heat exchangers in cooling water systems. Electrochemical methods such as anodic and cathodic polarization, impedance spectroscopy and solution analysis were used. Dezincification of brass was analyzed using atomic absorption spectroscopy. The composition of brass surface was analyzed using energy dispersive X-ray analysis (EDAX).

2. Experimental details

2.1. Materials

The chemical composition (wt. %) of the brass plate used in these tests was 65.3% Cu, 34.44% Zn, 0.1385% Fe, 0.0635% Sn and trace amounts of Pb, Mn, Ni, Cr, As, Co, Al and Sr as analyzed by optical emission spectrometry. The brass specimens were polished mechanically with different grades of silicon carbide papers (120–1200) and were thoroughly washed with double distilled water then degreased in acetone and



Scheme 1. The structures of benzotriazole derivatives.

dried [22]. The inhibitors *N,N*-dibenzotriazol-1-ylmethylamine and 2-hydroxy ethyl benzotriazole were synthesized according to the reported procedures [23, 24]. The solutions were prepared from analar grade chemicals using double distilled water. The structures of benzotriazole derivatives are shown in Scheme 1.

2.1.2. Synthesis of DBMA and HEBTA

Preparation of DBMA: 2% aqueous ammonia (21.2 ml, 25 mmol) was neutralized with acetic acid (Phenolphthalein). 1-Hydroxy methyl benzotriazole (5.96 g, 40 mmol) in methanol was then added (50 ml) and the mixture were kept at 25 °C for 5 h and then at -5 °C for 16 h. The precipitate was filtered off, washed with water and recrystallized from ethanol to give analytically pure DBMA [24].

Preparation of HEBTA: Benzotriazole (2.38 g, 20 mmol) was dissolved in 3.4 ml of acetaldehyde (20% aqueous solution) by gently warming and was kept at 25 °C. The product obtained was recrystallized with 1:1 mixture of chloroform and methanol [23].

2.2. Weight-loss studies

Measurements of weight changes were performed with rectangular brass coupons (5 cm × 3 cm × 0.3 cm). The coupons were immersed in 300 ml of 3% NaCl solution (pH=6.7) with and without inhibitors and allowed to stand for 5 days at room temperature. Afterwards, the coupons were rinsed with distilled water and adherent corrosion products were removed by dissolving in 1 M H₂SO₄ for 10 min. Then the coupons were rinsed with water, cleaned with acetone and dried [25]. Duplicate tests were conducted for each experiment. The percentage

of inhibition efficiency (IE%) over the exposure period was calculated using the following equation.

$$IE\% = \frac{CR - CR_{inh}}{CR} \times 100$$

where CR_{inh} and CR are the rate of corrosion of brass with and without inhibitors respectively.

2.3. Potentiodynamic polarization studies

The potentiodynamic polarization studies were carried out with brass strips having an exposed area of 1 cm². The cell assembly consisted of brass as working electrode, a platinum foil as counterelectrode and a saturated calomel electrode (SCE) as a reference electrode with a Luggin capillary bridge. Polarization studies were carried out using a potentiostat/galvanostat (model PGSTAT 12) and the data obtained were analyzed using the GPES software version 4.9. The working electrode was immersed in a 3% NaCl solution and allowed to stabilize for 30 min [26]. Each electrode was immersed in a 3% NaCl solution in the presence and absence of optimum concentrations of the inhibitors to which a current of 1.5 mA cm⁻² was applied for 15 min to reduce oxides. The cathodic and anodic polarization curves for brass specimen in the test solution with and without various concentrations of the inhibitors were recorded at a sweep rate of 1 mV s⁻¹. The inhibition efficiencies of the compounds were determined from corrosion currents using the Tafel extrapolation method.

2.4. Electrochemical AC impedance studies

AC impedance measurements were conducted at room temperature using an Autolab with frequency response analyzer (FRA), which included a potentiostat model PGSTAT 12. An ac sinusoid of ±10 mV was applied at the corrosion potential (*E*_{corr}). The frequency range of 100 kHz–1 mHz was employed. The brass specimen with an exposing surface area of 1 cm² was used as the working electrode. A conventional three electrode electrochemical cell of volume ~100 ml was used [27]. A saturated calomel electrode (SCE) was used as the reference and a platinum plate electrode was used as the counter. All the potentials reported here are with respect to SCE.

2.5. Solution analysis

During the anodic polarization, metal dissolution takes place releasing a considerable amount of metal ions from the material. Hence, the solutions were analyzed to determine the leaching characteristics of the brass alloys. The solution left after polarization measurements were analyzed for copper and zinc by atomic absorption spectrometry to measure the amount of Cu and Zn leached out from the alloys. The solutions containing the optimum concentration of the inhibitor were chosen. A blank solution containing no inhibitors was chosen

for comparison. The dezincification factor (z) was calculated using the relation

$$z = \frac{(\text{Zn/Cu})_{\text{sol}}}{(\text{Zn/Cu})_{\text{alloy}}}$$

where the ratio $(\text{Zn/Cu})_{\text{sol}}$ is determined from solution analysis and $(\text{Zn/Cu})_{\text{alloy}}$ is the weight-percent ratio of the elements in the alloy [6, 28].

2.6. Surface analysis of attacked metal alloy

The composition of the brass surface after polarization measurements was analyzed using energy dispersive X-ray analysis (EDAX).

3. Results and discussion

3.1. Weight-loss method

The results of weight-loss measurements are shown in Table 1. The inhibition efficiency increases with increase in inhibitor concentration. The maximum IE% of each compound was achieved at 150 ppm and a further increase in concentration showed only a marginal change in performance. Hence, the optimum levels of inhibitor concentration were found to be 150 ppm. The percentage IE of the compounds studied was in the following order.



3.2. Potentiodynamic polarization studies

The cathodic and anodic polarization curves of 65/35 brass in 3% NaCl solution with varying concentrations

Table 1. Inhibition efficiency for various concentrations of benzotriazole derivatives for the corrosion of brass in 3% NaCl obtained from weight-loss method

Inhibitor concentration/ppm	Corrosion rate/mm year ⁻¹ × 10 ⁻²	Inhibition efficiency/%
Blank	11.83	–
<i>BTA</i>		
50	5.42	54.18
100	4.56	61.45
150	2.98	74.81
200	3.12	73.63
<i>DBMA</i>		
50	4.81	59.34
100	3.89	67.11
150	1.52	87.15
200	1.58	86.64
<i>HEBTA</i>		
50	3.87	67.29
100	2.88	75.66
150	0.92	92.22
200	0.94	92.05

of BTA, DBMA and HEBTA are shown in Figures 1–4. The three distinct regions appearing in the anodic polarization curve were the active dissolution region (apparent Tafel region), the active-to-passive transition region and the limiting current region.

The kinetics and mechanism of anodic dissolution and film formation of brass in neutral chloride solution can be thought of as taking place via the reactions outlined below [29]. In the initial corrosion stage, zinc forms ZnO as a result of

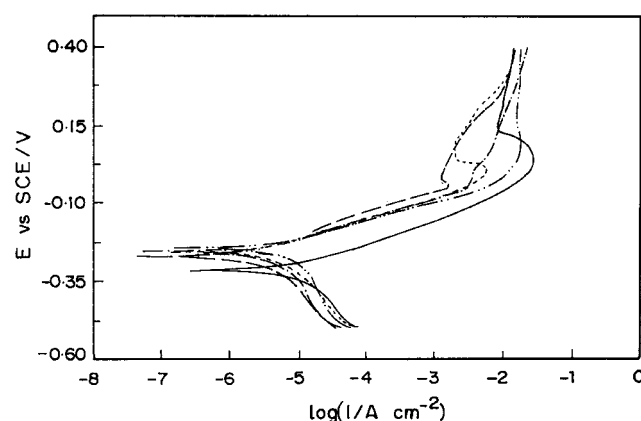


Fig. 1. Polarization curves for brass in 3% NaCl containing different concentrations of BTA: (—) Blank, (---) 50 ppm, (- · - · -) 100 ppm, (- - -) 150 ppm, (- - - - -) 200 ppm.

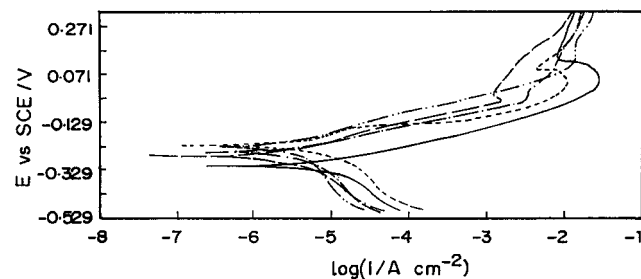


Fig. 2. Polarization curves for brass in 3% NaCl containing different concentrations of DBMA: (—) Blank, (---) 50 ppm, (- · - · -) 100 ppm, (- - -) 150 ppm, (- - - - -) 200 ppm.

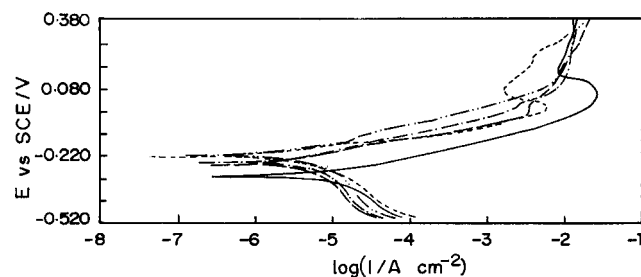


Fig. 3. Polarization curves for brass in 3% NaCl containing different concentrations of HEBTA: (—) Blank, (---) 50 ppm, (- · - · -) 100 ppm, (- - -) 150 ppm, (- - - - -) 200 ppm.

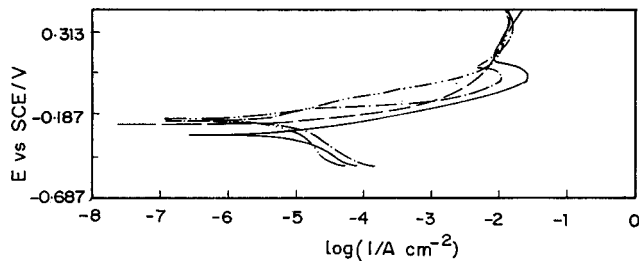
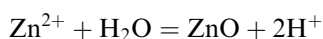
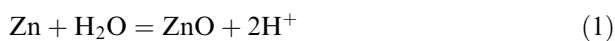


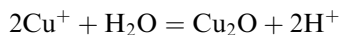
Fig. 4. Polarization curves for brass in 3% NaCl containing optimum concentrations of benzotriazole derivatives: (—) Blank, (----) BTA, (- · - · - ·) DBMA, (· · ·) HEBTA.



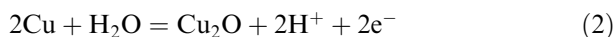
or



and copper forms Cu_2O as a result of



or



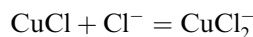
After the surface has become covered by both ZnO and Cu_2O , CuCl is formed on the surface by the reaction



which can then undergo the disproportionation reaction [30]



or dissolve with the formation of CuCl_2^- complexes [31, 32] via



It is evident that in the presence of inhibitor, the cathodic and anodic curves were shifted towards positive potential region and the shift was found to be dependent on inhibitor concentration. Table 2 illustrates the corresponding electrochemical parameters. The E_{corr} values were marginally shifted in the presence BTA, DBMA and HEBTA. This observation clearly indicated that the inhibitors control mainly the anodic reactions and thus act as anodic type inhibitors. The current density also decreased with increasing concentrations of the inhibitors. The inhibition efficiency was calculated from I_{corr} values [33].

$$\text{IE}\% = \frac{I_{\text{corr}} - I_{\text{corr(inh)}}}{I_{\text{corr}}} \times 100$$

where $I_{\text{corr(inh)}}$ and I_{corr} are the corrosion current density in the presence and absence of inhibitors, respectively.

The values of cathodic Tafel slope (b_c) and anodic Tafel slope (b_a) of benzotriazole derivatives are found to change with inhibitor concentration, which clearly indicates that the inhibitors controlled both reactions. The inhibition efficiency of BTA, DBMA and HEBTA attained a maximum value of 77.35, 89.66 and 94.31% at 150 ppm concentration, respectively. The values of inhibition efficiency increase with increasing inhibitor concentration, indicating that a higher surface coverage was obtained in a solution with the optimum concentration. The corrosion rate in blank solution was found to be $10.8 \times 10^{-2} \text{ mm year}^{-1}$ and it was minimized by adding the inhibitors to a lower value of 2.45×10^{-2} , 1.12×10^{-2} and $0.62 \times 10^{-2} \text{ mm year}^{-1}$ for 65/35 brass

Table 2. Electrochemical parameters and inhibition efficiency for corrosion of brass in 3% NaCl containing different concentrations of benzotriazole derivatives

Inhibitor Concentration/ppm	$I_{\text{corr}}/\mu\text{A cm}^{-2}$	$E_{\text{corr}}/\text{mV vs. SCE}$	$b_a/\text{mV (dec)}^{-1}$	$b_c/\text{mV (dec)}^{-1}$	Corrosion rate/mm year ⁻¹ × 10 ⁻²	Inhibition efficiency/%
Blank	8.61	-312	175	73	10.8	—
BTA						
50	3.83	-283	119	63	4.80	55.52
100	3.09	-265	108	60	3.88	64.11
150	1.95	-240	60	82	2.45	77.35
200	2.00	-256	70	84	2.51	76.77
DBMA						
50	3.18	-270	85	40	3.99	63.07
100	2.54	-261	59	35	3.19	70.50
150	0.89	-232	44	33	1.12	89.66
200	1.00	-235	46	38	1.25	88.39
HEBTA						
50	2.46	-258	73	39	3.09	71.43
100	1.79	-247	77	48	2.25	79.21
150	0.49	-225	42	35	0.62	94.31
200	0.56	-228	43	37	0.70	93.50

due to the adsorption of BTA, DBMA and HEBTA on the surface, respectively.

The inhibition efficiency of the compounds studied is due to donor–acceptor interactions between the π electrons of the inhibitor and the vacant d-orbital of copper surface or an interaction of inhibitor with already adsorbed chloride ions [34, 35]. The corrosion inhibition properties of BTA, DBMA and HEBTA are also due to the presence of heteroatoms such as N, O and π electrons in the aromatic nuclei. These factors play a vital role in the adsorption of the inhibitor.

HEBTA has the highest inhibition efficiency when compared to DBMA. The high solubility of HEBTA in 3% NaCl and the presence of an oxygen atom with a lone pair of electrons make HEBTA a very good inhibitor.

3.3. AC impedance studies

The corrosion behavior of brass in NaCl solution in the presence of benzotriazole derivatives was investigated by electrochemical impedance spectroscopy (EIS) at room temperature. Various impedance parameters such as charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and inhibition efficiency (IE) were calculated and are given in Table 3. The impedance diagrams were not perfect semicircles, which may be attributed to the frequency dispersion [21]. The charge transfer values (R_{ct}) were calculated from the difference in impedance at the lower and higher frequencies as suggested by Haruyama and Tsuru [36]. To obtain the double layer capacitance (C_{dl}), the frequency at which the imaginary component of the impedance is maximum ($-Z''_{max}$) was found and C_{dl} values were obtained from the following equation.

$$C_{dl} = \frac{1}{2\pi f(-Z''_{max})R_{ct}}$$

Nyquist plots of brass in inhibited and uninhibited NaCl solution containing optimum concentrations of benzotriazole derivatives are shown in Figure 5. The percentage inhibition efficiency (IE%) of corrosion of brass is calculated by R_{ct} as follows:

$$\text{Inhibition efficiency (IE\%)} = \frac{(R_{ct})^{-1} - (R_{ctinh})^{-1}}{(R_{ct})^{-1}} \times 100$$

Table 3. Impedance measurements and inhibition efficiency in 3% NaCl containing optimum concentrations of benzotriazole derivatives after immersion of 48 h

Inhibitors	$R_{ct}/\sim \text{cm}^2$	$C_{dl}/\mu\text{F cm}^{-2}$	Inhibition efficiency/%
Blank	1.889×10^4	0.415	–
BTA	1.845×10^5	0.068	89.75
DBMA	2.42×10^5	0.034	92.19
HEBTA	5.89×10^5	0.012	96.79

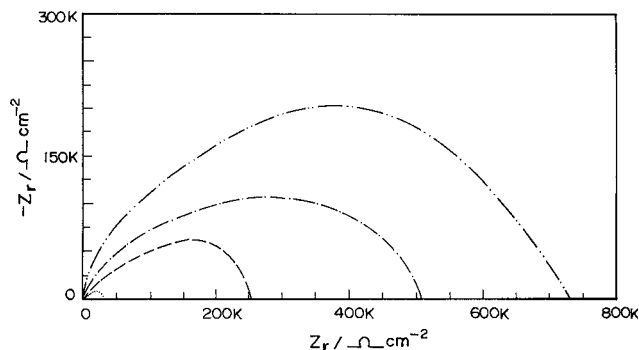


Fig. 5. Nyquist diagrams for brass in 3% NaCl containing optimum concentrations of benzotriazole derivatives after immersion of 48 h. (.) Blank, (-----) BTA, (- · - · -) DBMA, (- - - -) HEBTA.

where $R_{ct\text{ inh}}$ and R_{ct} are the charge-transfer resistance values with and without inhibitors respectively. After 48 h immersion, inhibition efficiency increases with increase in inhibitor concentration in 3% NaCl solution. The inhibition efficiency values determined using the polarization curves were lower than those determined by EIS. This difference is probably due the shorter immersion time in the case of the polarization measurements [37]. Impedance parameters derived from these investigations are given in Table 3. In the presence of optimum inhibitors concentration, R_{ct} values increased, whereas C_{dl} values tended to decrease. The tendency of decrease in C_{dl} , which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the benzotriazole derivatives function by adsorption at the metal-solution interface [38]. The change in R_{ct} and C_{dl} values was caused by the gradual replacement of water molecules by the anions of the NaCl and adsorption of the organic molecules on the metal surface, reducing the extent of dissolution [39].

3.4. Solution analysis

The results of solution analysis and the corresponding dezincification factor (z) in the presence and absence of benzotriazole derivatives at their optimum concentration level in 3% NaCl solution for 65/35 brass are given in Table 4.

Both copper and zinc were present in the solution. The copper/zinc ratio in solution was found to be smaller than that in the bulk alloy. This indicates that growth of the surface film and dissolution of the alloy were controlled by diffusion [32], which is related to the difference between the ionic radii of Zn^{+2} and Cu^{+} ions, 0.07 and 0.096 nm, respectively. The results indicate that the inhibitors are able to minimize the dissolution of both copper and zinc. The percent inhibition efficiency against the dissolution of zinc was correspondingly higher as compared to the dissolution of copper. This suggests that the benzotriazole derivatives efficiently prevent the dezincification of 65/35 brass

Table 4. Effect of optimum concentrations of benzotriazole derivatives on the dezincification of brass in 3% NaCl solution

Inhibitors	Solution analysis		Dezincification factor (z)	Percent inhibition	
	Cu /ppm	Zn /ppm		Cu	Zn
Blank	0.68	16.32	44.57	–	–
BTA	0.13	2.46	39.59	81.6	84.91
DBMA	0.09	1.69	34.01	86.47	89.67
HEBTA	0.06	0.87	27.88	91.40	94.66

Table 5. Surface composition (wt.%) of brass in 3% NaCl after polarization with optimum concentrations of inhibitors

Inhibitors	Cu/wt.%	Zn/wt.%	Cl/wt.%
Alloy	65.3	34.44	–
Blank	59.62	23.23	17.15
BTA	63.46	29.65	6.89
DBMA	64.43	32.86	2.71
HEBTA	65.14	33.83	1.03

in 3% NaCl solution, which is also reflected in the values of the dezincification factor.

3.5. Surface composition analysis

The surface composition (wt.%) of the alloy in the presence and absence of inhibitors is given in Table 5. In the absence of inhibitors, the wt. % of Cu and Zn present in the surface layer were reduced due to the leaching of metal ions in the 3%NaCl solution. Moreover, the higher concentration of chloride ions on the surface shows the penetration of Cl⁻ ions into the alloy. However, in the presence of DBMA and HEBTA, the wt.% of Cu and Zn are closer to that of the bulk alloy composition. Based on the surface analysis, these inhibitors exhibited excellent inhibition efficiency in sodium chloride solution.

4. Conclusions

The investigated compounds show excellent performance as corrosion inhibitors in sodium chloride solution. The inhibition efficiencies of BTA derivatives follow the order: HEBTA > DBMA > BTA. Polarization studies showed that benzotriazole derivatives behave mainly as anodic inhibitors for brass in chloride solutions. They decrease the anodic reaction rate more strongly than the cathodic reaction and render the open circuit potential of brass more positive in NaCl solutions. Impedance studies indicated that R_{ct} values increased, while C_{dl} values decreased in the presence of the inhibitors. Solution analysis showed that the inhibitors employed in the present investigation are able to minimize the dissolution of both copper and zinc. These are excellent agents for inhibiting dezincification of

brass. The inhibitors readily adsorb on the metal surface at the corrosion potential and form a protective complex with the Cu^I ion, preventing brass from corrosion.

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